STUDIES OF SOME 2,4-LUTIDINE DERIVATIVES

BY

FRANCIS WARREN BLODGETT

A. B., Oberlin College, 1943

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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INTRODUCTION

A compound identified as a 2-pyridonedicarboxylic acid has been prepared by Sampson (1) by hydrolysis of the adduct of cinnamalaniline and methyl acetylenedicarboxylate, followed by ammonolysis of the intermediate 1-phenyl-2-pyridonedicarboxylic acid. In connection with further investigations of these reactions, it was of interest to prepare a number of new compounds derived from 2,-4-lutidine and to investigate their oxidation to the corresponding substituted lutidinic acids.

DISCUSSION OF RESULTS

6-Amino-2,4-lutidine was prepared by amination of 2,4-lutidine by sodium amide according to the method described by Chichibabin and Seide (2) as modified by Leffler (3). The position of the amino group was determined by diazotization of the compound in dilute sulfuric acid solution; a product identical with an authentic sample of 4,6-dimethyl-2-pyridone was obtained.

6-Phthalimido-2,4-lutidine was prepared by fusing 6-amino-2,4-lutidine with phthalic anhydride. Dichromic acid oxidation of this compound destroyed the pyridine nucleus and the usually stable phthalimido ring; phthalic acid was isolated from the reaction mixture.

6-Bromo-2,4-lutidine was prepared from 6-amino-2,4-lutidine by diazotization in hydrobromic acid solution in the presence of bromine and an excess of sodium nitrite by the method of Craig (4) for 2-bromopyridine, and 6-chloro-2,4-lutidine was prepared from 4,6-dimethyl-2-pyridone by reaction with phosphorus pentachloride (5). Oxidation of 6-chloro-2,4-lutidine with either potassium permanganate or dichromic acid afforded 4-carboxy-6-chloro-2-picoline but no dicarboxylic acid; 6-bromo-2,4-lutidine was recovered unchanged from an attempted oxidation with hot nitric acid.

6-Ethoxy-2,4-lutidine (6) was prepared by heating 6-bromo-2,4-lutidine with sodium ethoxide. Oxidation with potassium permanganate gave a product tentatively identified as 6-ethoxylutidinic acid.

1-Hydroxy-2,4-dimethylpyridinium chloride was prepared by oxidation of 2,4-lutidine with monoperphthalic acid and treatment of the intermediate 1-hydroxy-2,4-dimethylpyridinium phthalate with hydrochloric acid. When this compound was treated with phosphorus pentachloride under the conditions reported by Meisenheimer (7) to afford 4-chloropyridinium chloride from 1-hydroxypyridinium chloride, the expected 6-chloro-2,4-lutidine was not obtained, but instead the hydroxyl group was eliminated and 2,4-lutidinium chloride resulted.

2,4-Distyrylpyridine (8) was prepared by heating 2,4-lutidine with benzaldehyde in the presence of zinc chloride. Nitric acid oxidation proceeded smoothly and lutidinic acid and 4-nitrobenzoic acid were isolated from the reaction mixture. The corresponding dibenzylidene derivative of 6-bromo-2,4-lutidine, sought as an intermediate for the preparation of 6-bromolutidinic acid, could not be prepared by heating 6-bromo-2,4-lutidine with benzaldehyde and zinc chloride in a Carius tube.

2,4-Dicarbomethoxy-1-methylpyridinium methosulfate, prepared by heating methyl lutidinate with methyl sulfate, gave an intense red color when its aqueous solution was made alkaline. The color was discharged reversibly by the addition of dilute acid. This reaction is probably analogous to the ring cleavage in alkaline solution of 1-(2,4-dinitrophenyl)-pyridinium chloride, depending on the presence of strong electron-withdrawing groups.

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VITA

The author was born in South Bend, Indiana, on August 14, 1922. He attended the public schools of Albany, Tarrytown and St. Albans, New York, and graduated from Jamaica (New York) High School in 1939. He entered Oberlin College in the fall of the same year, and graduated with the A. B. degree in 1943. After two and one-half years in the U. S. Navy, he entered the Graduate College of the University of Illinois in March, 1946, where he held teaching assistantships from September, 1946, to June, 1948.

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